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수분함량에 따른 생선단백질의 동적특성에 관한 연구

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Dynamic Properties of Surimi-based Seafood Product as a Function of Moisture Content

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Abstract

The changes in the rheological dynamic properties of Alaska pollack surimi gel such as storage modulus (G'), loss modulus (G") and complex viscosity (η) upon the different storage temperatures (5~25°C) were measured using a Bohlin Rheometer as a function of moisture content (75~80%), and analyzed by time-temperature superposition theory with storage modulus. The linear viscoelastic region was determined by a stress sweep, and oscillatory measurements (0.01~10 Hz) were carried out within a linear viscoelastic ranges. As the storage temperature increased from 5 to 25°C and moisture content was increased from 75 to 80%, the lower values of each dynamic properties were observed. The master curve was constructed by moving each storage modulus curve horizontally on the basis of reference temperature (15°C) and reference moisture content (77.5%) using shift factors. Activation energies of each surimi gel were calculated as a function of temperature and moisture content, and revealed that the addition of moisture content in surimi gel caused higher activation energy values but sharply decreased it to a lower level as storage temperature was increased.

Key words: Surimi, storage modulus, master curve, and activation energy

Introduction

Surimi gel is a heated fish myofibrillar protein and is gradually increased in its consumption during last decade (Park, 1995a). The textural quality of surimi seafood is commonly evaluated by rheological properties of final cooked gel properties such as failure stress and strain (Montejano *et al.*, 1985: Hamann, 1992; Howe *et al.*, 1994; Yoon *et al.*, 1996), or static properties during heating period such as compressive stress, rigidity, and elastic modulus (Hamada and Inamasu, 1983; Niwa *et al.*, 1987, 1988; Sano *et al.*, 1990; Nowsad *et al.*, 1994). However, rheological properties of surimi seafood were dramatically changed due to storage temperature and storage time (Niwa *et al.*, 1987). Howe *et al.* (1994) found that even test temperature affected final gel properties, in that surimi gels tested at 50°C were more brittle than those tested above 50°C, and changes in rheological properties of gels at the tested temperatures were dependent upon fish species (Park, 1995b).

Moisture content also considered to be of greater important parameter influencing mechanical properties such as viscoelastic responses (Herum *et al.*, 1979; Pappas and Rao,1989), microbiological stability as well as rupture properties of surimi seafood (Yoon *et al.*, 1996), and energy absorption (Hoag, 1972). Herum *et al.* (1979) studied the viscoelastic behavior of soybean due to temperature and moisture content, showed a single master curve

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Corresponding author: Byung-Yong Kim, Department of Food Sci. and Tech., Kyung Hee University, Yongin, 449-701, Korea represented the relaxation modulus of whole soybean. Pappas and Rao (1989) also constructed the single master response curve using the temperature and moisture shift factors. Also, viscoelastic properties changes of other food such as ovalbumin gel (Gringberg *et al.*, 1988), whey protein gel (Katsuta *et al.*, 1990), rice starch (Hong *et al.*, 1992) and soybean curd (Jang *et al.*, 1995) were studied for the viscoelastisity and time-temperature superposition application. Protein foods like a surimi gel also have both elastic and viscous characteristics when mechanically stressed. These viscoelastic properties of surimi gel were also affected by various storage conditions. However, changes in viscoelastic properties of surimi gel during storage have not been thoroughly studied. Therefore, the overall objective of this study was to measure the dynamic property changes during storage as a function of moisture and storage temperature, and to demonstrate the temperature and moisture dependency of viscoelasticity of surimi seafood from the master curve obtained using shift factor.

Material and Methods

Material

A high grade (FA) of surimi from Alaska pollack (Arctic Storm, Seattle, WA) was used to evaluate the dynamic rheological properties. Block of surimi (700 g) was stored at -25°C until used. The moisture content of pollack surimi was 75%, measured by AOAC method (1990) and moisture content of surimi samples were adjusted to 75, 77.5 and 80% using an ice.

Measurement of dynamic rheological properties

Preparation and measurement of dynamic viscoelastic properties of surimi gel were directly performed in a Bohlin Rheometer (Model CS-50, Bohlin instrument, Crenbery, NJ), equipped with an automatic controlled by circulating water-bath and connected to a PC computer. The measuring units were the cone (degree=4°, diameter=40 mm) and plate (diameter=60 mm), and solvent trap was placed on the top of the plate to minimize the moisture loss. The frequency sweep experiment at different storage temperatures (5~25°C) was conducted with surimi gel made from different moisture contents (75~85 %). Linear viscoelastic range at each moisture content was obtained from stress sweep (1~1500 Pa).

Time-temperature superposition theory using shift factor

The time-temperature superposition theory was applied to investigate the storage temperature dependency of storage modulus (G') of surimi gel, according to Jang *et al.* (1995). The temperature of surimi gel was controlled by circulating water-bath and dynamic properties of surimi gel were measured at the specific storage temperature (5~25°C). Shift factor (a_T) indicating the temperature dependency was calculated by equation 1 (Katsuta and Kinsella, 1990).

$$a_T=t_T/t_{T_o} \tag{1}$$

where t_T is the time required to reach a particular response at temperature T, and t_{T_o} is the time required to reach the same response at reference temperature T_o and the G' value at the 0.1 Hz was used as a reference response. The correlation between a_T and $(T-T_o)$ was expressed as follows (Ferry, 1980).

$$\mathrm{Log}\ a_T=-C_1\cdot(T-T_o)/[C_2+(T-T_o)] \tag{2}$$

where C_1 and C_2 are the temperature dependent constants and $(T-T_o)$ is the difference between observed temperature and reference temperature.

Rearranged the equ. (2) and then, following equation was obtained.

$$-(T-T_o)/\mathrm{Log}\ a_T=C_2/C_1+(T-T_o)/C_1 \tag{3}$$

Linear relationship between the $-(T-T_o)/(\mathrm{Log}\ a_T)$ versus $(T-T_o)$ indicated that the surimi gels at these ranges of moisture contents followed WLF (Williarm-Landel-Ferry) equation and then C_1 and C_2 were obtained from the slope and intercept.

Based on the values of C_1 and C_2 the activation energies were obtained from the equ. (4) as a function of moisture.

$$\triangle H=(2.303.R.C_1.T.T_o)/[C_2+(T-T_o)] \tag{4}$$

Results and Discussion

Measurement of viscoelastic properties of surimi gel

The typical viscoelastic properties of Alaska pollack surimi gel (75% moisture content) at different frequencies was shown in Fig. 1. Storage modulus (G') is defined as the stress in phase with the strain in a sinusoidal deformation divided by the strain and is a measure of the energy stored and recovered per cycle, whereas loss modulus (G") is defined as the stress 90° out of phase with the strain divided by the strain and is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation (Ferry, 1980). Log G' value showed the range of 5.27~5.6 Pa at all frequency levels (0.01~10 Hz) and the slope was approached to zero, represented the phase angle between stress and strain approaches 0 as the stored energy per cycle of deformation becomes predominant, compared with that of dissipated as heat (Hamann, 1992) In such regions G" values (4.7~4.72) tended to be considerably less than G' value, represented surimi gel is corresponded to the rubber-like gel characteristics, showing a large deformability with essentially complete recovery, and can be treated by the theory of rubber-like elasticity (Ferry, 1980, Katsuta and Kinsella, 1990).

The dynamic viscosity can be described by the ratio of stress divided by the rate of strain at each frequency. Dynamic viscosity was inversely proportional to the frequency in regions where G" was flat, reached values many orders of magnitude smaller than those at the lower frequencies (Fig. 1). The decrease in complex viscosity exhibited a viscous flow of uncross-linked polymer above the glass transition temperature (Ferry, 1980) and flow may result from rearrangement of rupture of temporary cross-links between proteins and from flow of water in the polymer. However, since viscosity is related to uncross-linked viscous material, but surimi gel has an infinitive viscosity value and many cross-linked protein bonds are developed during heating and cooling, only G' value of surimi gel was selected in this study for the time-temperature superposition.

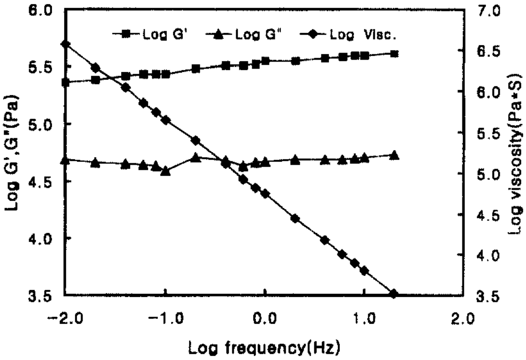

Fig. 1. Dynamic properties of Alaska pollack surimi gel (75% moisture content) at different frequencies.

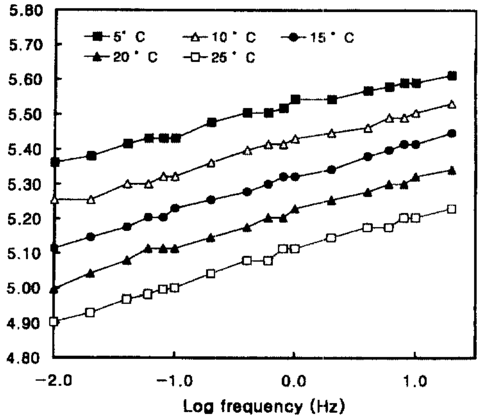

Fig. 2. The changes in storage modulus values at different storage temperatures (5~25°C).

The change in G' values at different storage temperatures (5~25°C) was shown in Fig. 2. Each value was strongly temperature dependent in that the magnitudes of G' values were increased at all frequency levels as storage temperatures were lower from 25 to 5°C. Zoon *et al.* (1990) measured the stress relaxation of skim milk gel and reported that stronger gel was formed at lower storage temperature, and Colwell (1969) demonstrated the formation of stronger wheat starch gel at lower storage temperatures and explained this phenomenon as a crystallization of starch, Generally, viscoelastic properties for many food products, such as whey protein (Katsuta and Kinsella, 1990), pectate (Michell and blanshadrd, 1976), cow pea (Pappas and Rao, 1989) and soybean (Herum *et al.*, 1979), were decreased with increasing storage temperatures.

Construction of master curve using shift factors

The time-temperature superposition theory was applied to demonstrate storage modulus (G') at larger ranges of frequencies from short frequency measurements at various temperatures. When the G' value at 15°C was set as a reference response and

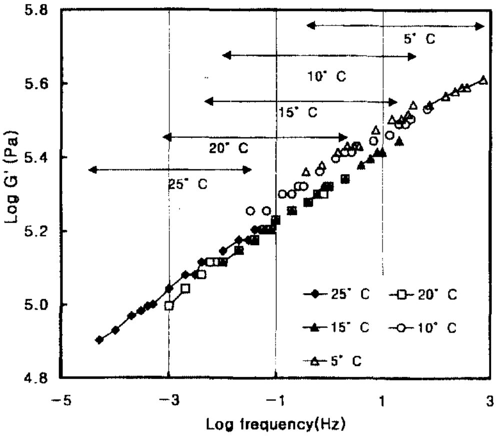

Fig. 3. Master curve of surimi gel having 75% moisture content superposed on the reference temperature curve (15°C).

other curves were shifted along the logarithmic frequency scale, a single master curve of surimi gel was constructed, based on the 15°C and 75% moisture content (Fig. 3). The shift factor at the reference temperature was 1, and the shift factor was larger than 1 at the storage temperature lower than 15°C, and was smaller than 1 at the storage temperature higher than 15°C (Jang *et al.*, 1995). The single master curve of surimi gel showed a linearly temperature-dependency of storage modulus with larger frequency scales. Katsuta and Kinsella (1990) demonstrated the master curve for the temperature dependency of whey protein gel, and temperature dependency of whey protein gel was related to the concentration of protein.

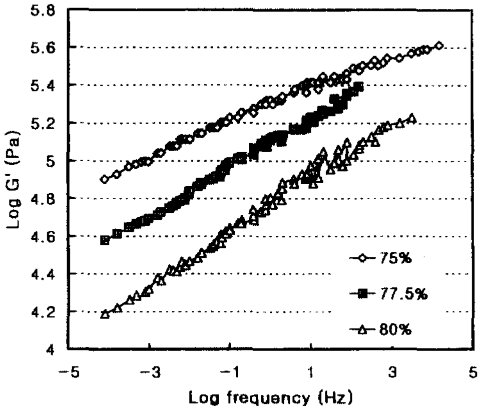

Fig. 4. Three master curves of surimi gel at different moisture contents obtained using each different temperature shifting factors.

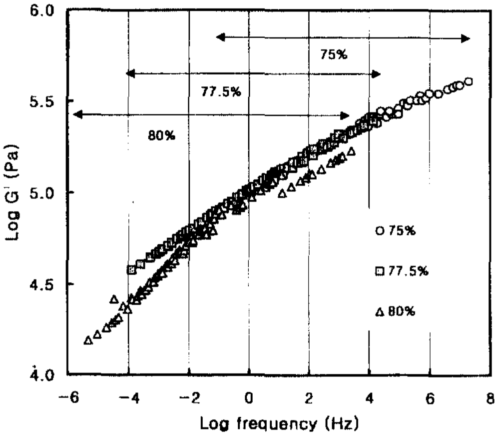

Fig. 5. The single master curve of surimi gel as a function of frequency at a reference temperature (15°C) and reference moisture content (77.5%).

Three master curves of surimi gel at different moisture contents were obtained from the same calculation using each different temperature shift factors (Fig. 4). An increase in moisture content from 75 to 80% in surimi gel produced lower storage modulus at all storage temperature ranges, and the slope (G'/frequency) at the higher moisture content (80%) was steeper than that of lower moisture (75%), indicating the more rubber-like gel product at lower moisture contents in surimi gel. The storage modulus master curves for each moisture content were converted to a single master curve by using the moisture shift factor, with 77.5% as the reference moisture content (Fig. 5). Thus three curves were reduced to a single mater curve, which represented both temperature and moisture effect on the storage modulus of surimi gel. Moisture shift factor was plotted as a function of moisture content to verify the moisture-time superposition (Fig. 6), and showed a linear relationship between moisture shift factor and moisture content (corr.=0.995), like a linear relationship between temperature shift factor and temperature (Fig. 7). Herum *et al.* (1979) and Pappas and Rao (1989) demonstrated the master curve as a function of temperature and moisture content using soybean and cow peas, respectively and both implied that these agricultural products are thermo- and hydro-rheologically simple biological materials. Since surimi gel showed a

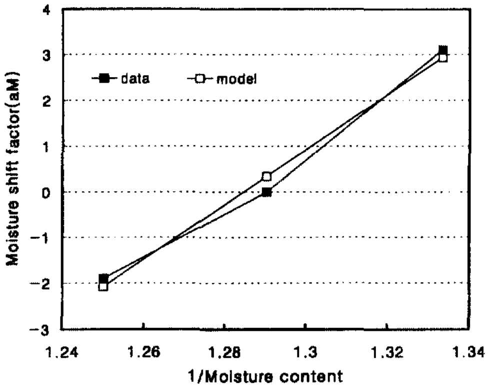

Fig. 6. Linear relationship between moisture shift factor (aM) and the moisture content (1/M) of surimi gel (75% moisture).

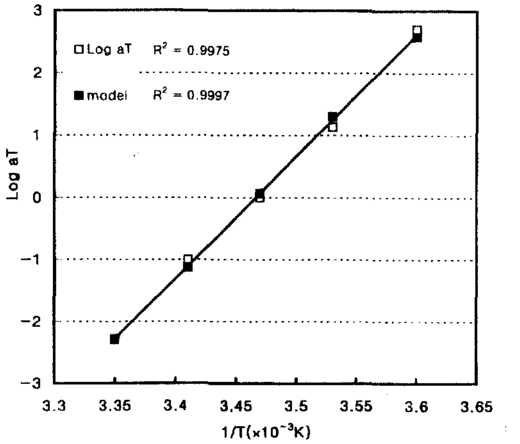

Fig. 7. Linear relationship between temperature shift factor (a_T) and the absolute temperature (1/T) of surimi gel.

highly homogeneity and isotropic behavior, compared to other biomaterial the time-temperature superposition theory could be further extended to obtain the activation energy.

Activation energy using WLF equation

Generally, activation energy (△H) was obtained from the slope between shift factor and temperature. However, the activation energy of high molecular materials such as soybean curd (Jang *et al.*, 1995), whey protein (Katsuta and Kinsella, 1990), alginate gel (Mitchel and Blamschard, 1976) and k-carrageenan gel (Watase and Nishinari, 1981) were changed with an increasing temperature. Thus, the activation energy was obtained from the storage modulus of surimi gel based on the time-temperature superposition theory (Williarms *et al.*, 1955).

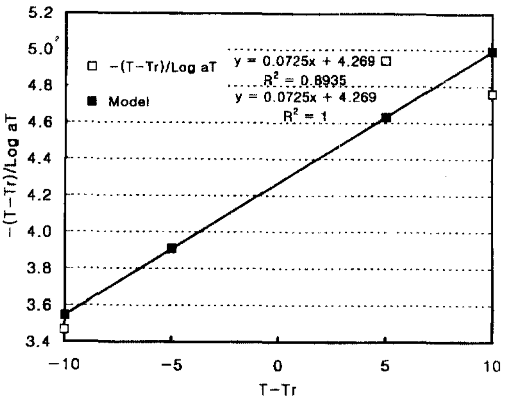

Fig. 8. -(T-T_o)/Loga_T vs (T-T_o) plot to determine the coefficient values (C_1 and C_2).

According to the equ. 3 the linear relationship (corr.=0.97) was obtained from the -(T-T_o)/Loga_T vs (T-T_o) plot (Fig. 8). From the slope (1/C_1) and intercept (C_2/C_1) in Fig. 8, C_1 and C_2 values were calculated at different moisture contents (Table 1). As the moisture increased from 75 to 80% both C_1 and C_2 values were decreased from 14.3 to 3.35, and 61.1 to 17.8, respectively. Using each C_1 and C_2 values at different moisture contents, the activation energy of surimi gel as a function of temperature was calculated using the equation 4 (Table 2). In the surimi gel contained 75% moisture content, the activation energy changed from 92 to 83 kcal/mol as the temperature increased from 5 to

Table 1. Constant values of C_1 and C_2 in WLF equation at different moisture content of surimi gel

Moisture (%)	C_1	C_2
75	14.3	61.1
77.5	11.5	52.1
80	3.35	17.8

Table 2. Activation energy changes as a function of moisture content in surimi gel at different moisture contents

Temperature (°C)	Moisture content (%)		
	75	77.5	80
5	92	100	157
10	89.5	91.5	97
15	87	83	71
20	85	77.5	56
25	83	72	45

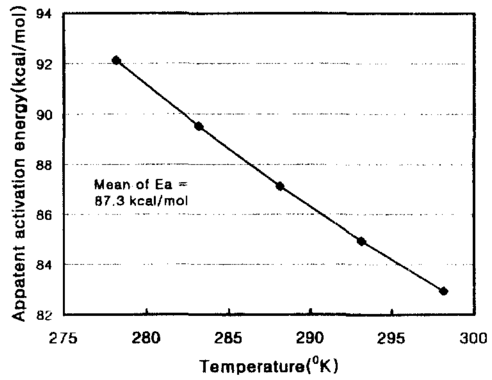

Fig. 9. Effects of temperature on apparent activation energies of surimi gels made with 75% moisture content.

25°C (Fig. 9). Further increasing the moisture to 77.5 % and 80%, the activation energy changed from 100 to 72 kcal/mol and from 158 to 45 kcal/mol, respectively, as the storage temperature increased from 5 to 25°C (Table 2). This indicated that addition of moisture content in surimi gel caused higher activation energy, but sharply decreased activation energy to a lower level as storage temperature was increased. The decrease in the activation energy at the higher storage temperature reflected the non covalent bond like a hydrogen bonding which has a predominant force at the lower storage temperatures (Hamann, 1992). The abrupt reduction of activation energy due to higher moisture content revealed that compositional change in surimi gel affected the activation energy which is intrinsic value in food systems.

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